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Trueblood

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[54] **ELECTROLESS GOLD PLATING ON REFRACTORY METALS**

[75] Inventor: **Richard Kent Trueblood,** Leucadia, Calif.

[73] Assignee: **Ceramic Systems,** San Diego, Calif.

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[52] **U.S. Cl.** ..... **117/50,** 106/1, 117/130 E, 117/160 R

[51] **Int. Cl.** **C23c 3/02**

[58] **Field of Search** .... 117/50, 47 R, 130 E, 160 R, 117/213, 35 S; 106/1; 29/199; 204/46, 38 B

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Primary Examiner—Charles E. Van Horn
Assistant Examiner—Michael W. Ball
Attorney, Agent, or Firm—Ronald E. Grubman

[57] **ABSTRACT**

For the electroless gold plating of metals, including refractory metals such as molybdenum, tungsten, columbium, and cobalt, a process is provided which includes activating the metal with an alkaline descaler followed by a dilute acid, and immersing the metal in a plating bath which is composed of a soluble gold salt, an organic chelating compound, a non-ammoniacal organic buffering and complexing agent, and a non-ammoniacal alkali hydroxide.

6 Claims, No Drawings

ELECTROLESS GOLD PLATING ON REFRACTORY METALS

BACKGROUND AND SUMMARY OF THE INVENTION

This invention relates to improvements in the process of electroless depositing of soft, ductile gold on metals, and particularly on refractory metals by which we mean, for example, such metals as molybdenum, tungsten, columbium, and cobalt. Heretofore, electroless depositing of gold on refractory metals has been difficult. Among the electroless plating process known in the prior art, plating solutions are used which include an organic chelating agent and an ammonium buffering agent. The ammonium buffering agent serves the dual purposes of regulating the pH of the bath and exerting a complexing action to complex some of the replaced metal ions from the surface of the metal being plated. When used to plate refractory metals such as molybdenum, tungsten, columbium, or cobalt, however, solutions of this kind could only deposit pure gold to thicknesses of a few microinches. The deposits obtained were of coarse texture, dark orange to brown in color, mottled in appearance, uneven in distribution, and lacking in adherence. These problems have rendered the heretofore available electroless gold solutions completely unsatisfactory for depositing gold films on refractory metals such as the metals mentioned above.

It is therefore the object of this invention to provide an electroless plating process capable of providing pure, soft, ductile gold of uniform yellow appearance to any desired thickness up to approximately 200 microinches, on metal substrates including substrates of the metals molybenum, tungsten, columbium, and cobalt, or on previously plated gold substrates.

The present invention achieves this object by providing a plating bath composed of a soluble gold salt such as the double cyanide of an alkali metal (e.g. potassium gold cyanide), an organic chelating compound (e.g. the tetra sodium salt of ethylenediaminetetraacetic acid tetrahydrate), a non-ammoniacal organic buffering and complexing agent (e.g. sodium potassium tartrate, "Rochelle Salt"), and a non-ammoniacal alkali hydroxide (e.g. sodium hydroxide). In the aforementioned bath, the soluble gold salt serves as a source of gold ions. The organic chelating compound serves to tie-up, or chelate, some of the undesirable metal ions which would otherwise contaminate the plating bath. These undesirable metal ions may be introduced into the bath as impurities in the plating chemicals, as reaction products during the plating process, or by accidental contamination through "drag-in" following cleaning and activation prior to the plating process. The alkali hydroxide serves to establish the range of pH necessary for operation of the bath, and the organic buffering and complexing agent serves to regulate the pH of the bath within the established range. To achieve good plating results, the above-described plating bath is used to plate metals which have first undergone an activating sequence which includes immersion of the metals in an alkaline descaler followed by an acid rinse. This procedure provides a suitable surface for the subsequent plating.

The present invention may be used whenever and wherever a gold protective layer on metals is desired or required. The invention has a potentially wide application in the fields of electronics, wherein powders of the refractory metals are sintered to ceramic insulators and subsequently gold plated to allow their brazing to metal members. Sintered metal powders are also used in hybrid microelectronics wherein these powders are overplated with gold and act as electrical conductors on ceramic substrates. This invention would be of incalculable value as an overplating for these sintered metal powders in that it would allow extremely uniform plating over all metallized areas.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In accordance with the preferred embodiment, the metal to be plated is first subjected to an activating treatment in preparation for immersion in a plating bath. The activating, or cleaning process includes first soaking the metal in a hot alkaline descaler (e.g. Isoprep 180 manufactured by Allied Kelite Products Inc.) at a temperature of between 80°C and 100°C. The metal is then rinsed in deionized water, and further rinsed in a hot dilute acid solution (e.g. a 20–50% hydrochloric acid solution) at a temperature of between 80°C and 100°C. A final rinse is performed using boiling deionized water.

After the metal to be plated has undergone the above-described activation treatment, it is immersed in a plating bath which includes a soluble gold salt (e.g. potassium gold cyanide) present in amounts ranging from 2 to 10 grams per liter with 4–5 grams per liter preferred, which serves as the source of supply for gold ions. Other soluble gold salts may be also used (e.g. sodium gold cyanide) but the potassium salt is preferred and more commercially available.

An organic chelating compound (e.g. tetra sodium ethylenediaminetetraacetate tetrahydrate) is present in amounts ranging from 10–50 grams per liter, with 20 grams per liter being preferred, and serves to tie-up or chelate undesirable metal ions which may be introduced into the bath. Other chelating compounds may also be used (e.g. ethylenediamine or triethlanolamine) but tetra sodium ethylenediaminetetraacetate tetrahydrate is preferred and readily available.

A non-ammoniacal organic buffering and complexing agent, for example an alkali metal salt of a weak acid such as sodium potassium tartrate, is present in amounts ranging from 25–100 grams per liter, with 55–70 grams per liter being preferred, and serves to regulate the bath pH to maintain the proper range for best plating efficiency. Increasing the amount of buffering and complexing agent decreases the rate of gold deposition but produces a finer-grained and brighter deposit. Decreasing the amount of buffering and complexing agent increases the gold deposition rate but leads to a coarse-grained slightly orange deposit. Other non-ammoniacal buffereing and complexing agents may be used (e.g. sodium or potassium citrate) but "Rochelle Salt," sodium potassium tartrate, is preferred.

A non-ammoniacal alkali hydroxide (e.g. sodium hydroxide) is present in amounts ranging from 5 to 50 grams per liter, with 8–18 grams per liter being preferred, and serves to establish the pH necessary for operation of the bath. Increasing the amount of the alkali hydroxide increases the gold deposition rate but oxidizes the metal substrate through chemical attack and leads to poor plating adherence on molybdenum, columbium, and tungsten. Oxidation is not as critical a

problem when plating cobalt, and a higher alkali hydroxide concentration is desirable, 30 grams per liter being preferred. Other nonammoniacal alkali hydroxides may be used (e.g. potassium hydroxide) but sodium hydroxide is preferred. Under no conditions should ammonium hydroxide or the salts thereof be added in place of or in addition to the alkali hydroxides. Doing so "poisons" the bath so that the rate of gold deposition is greatly reduced if not halted altogether.

The following are examples of electroless plating processes according to the invention, based on one liter of plating solution:

Example 1

	Grams/Liter
Potassium gold cyanide	4
Tetra sodium ethylenediaminetetraacetate tetrahydrate	20
Sodium potassium tartrate	58
Sodium hydroxide	18
Deionized water	Remainder

The pH of the bath was 13.2–13.5. The bath was used to plate tungsten metallized ceramic circuit boards after first undergoing the following cleaning sequence:

Alkaline descaler at 95°C	15 min.
Deionized water rinse	1 min.
20% hydrochloric acid rinse at 85°C	5 min.
Deionized water rinse at 100°C	5 min.

The circuit boards were then immersed in a beaker of the plating solution and remained there at 100°C for 35 minutes. On removing the circuit boards from the bath and subsequently rinsing and drying, the thickness of gold deposited, as determined by the Weight-Area Method, was approximately 120 microinches.

Example 2

	Grams/Liter
Potassium gold cyanide	4
Tetra sodium ethylenediaminetetraacetate tetrahydrate	20
Sodium potassium tartrate	58
Sodium hydroxide	30
Deionized water	Remainder

The pH of the bath was 13.4–13.7. The bath was used to plate tungsten metallized ceramic circuit boards which had been given an electroless cobalt overplate of approximately 40 microinches thickness. After the circuit boards had been removed from the cobalt plating bath, they were subjected to the cleaning sequence of example 1 above and transferred to the above gold plating bath. The circuit boards remained in the bath at 100°C for 45 minutes. On removing the circuit boards from the bath and subsequently rinsing and drying, the thickness of gold deposited, as determined by the Weight-Area Method, was approximately 100 microinches.

Example 3

	Grams/Liter
Potassium gold cyanide	2
Tetra sodium ethylenediaminetetraacetate tetrahydrate	20
Sodium potassium tartrate	70
Sodium hydroxide	8
Deionized water	Remainder

The pH of the bath was 13.0–13.2. The bath was used to plate columbium metal plates after first undergoing the cleaning sequence of Example 1 above.

The columbium plates were allowed to remain in the solution for 15 minutes at 100°C. Upon their removal from the bath and after subsequent rinsing and drying, the thickness of gold deposited, as determined by the Weight-Area Method, was approximately 200 microinches.

Example 4

	Grams/Liter
Potassium gold cyanide	4
Tetra sodium ethylenediaminetetraacetate tetrahydrate	20
Sodium potassium tartrate	58
Sodium hydroxide	18
Deionized water	Remainder

The pH of the bath was 13.2–13.5. The bath was used to plate molybdenum metal plates after first undergoing the cleaning sequence of Example 1 above. The molybdenum plates were allowed to remain in the solution for 30 minutes at 100°C (boiling). Upon their removal from the bath and after subsequent rinsing and drying, the thickness of gold deposited, as determined by the Weight-Area Method, was approximately 55 microinches.

Although the plating baths in the above examples were operated at the boiling point (approximately 100°C), temperatures as low as 80°C result in satisfactory deposits. Operation at the boiling point has the advantage, however, of providing continuous bath agitation by virtue of the boiling point action, thereby increasing the deposition rate. Thus, less time is required to obtain equivalent deposition thickness when the process is operated at the boiling point.

In the above examples, the gold deposits obtained had the yellow-color of pure gold and were of 24 karat purity.

I claim:

1. A method for plating refractory metals comprising the steps of:

activating the metal to be plated by immersing it in an alkaline descaler at a temperature in the range of 80°–100°C, rinsing the metal in deionized water, rinsing the metal in a dilute acid at a temperature in the range of 80°–100°C, and rinsing the metal in boiling deionized water; and

immersing the metal in an electroless gold plating bath consisting essentially of water, about 2 to 10 grams per liter of a soluble gold salt selected from the group consisting of potassium gold cyanide and sodium gold cyanide, about 10 to 50 grams per liter of an organic chelating compound, about 25 to 100 grams per liter of a non-ammoniacal alkali metal salt of a weak acid to serve as a buffering and complexing agent, and a non-ammoniacal alkali metal hydroxide in an amount sufficient to bring the pH of the bath to between about 13 to 14.

2. A method as in claim 1 wherein the step of rinsing the metal in a dilute acid comprises the step of rinsing

the metal in a hydrochloric acid solution in the range of 20–50 vol. percent.

3. A method as in claim 1 wherein the step of immersing the metal in an electroless gold plating bath including a non-ammoniacal alkali metal salt of a weak acid comprises the step of immersing the metal in an electroless gold plating bath including a non-ammoniacal alkali metal salt of a weak acid selected from the group consisting of sodium potassium tartrate, sodium citrate, and potassium citrate.

4. A method as in claim 1 wherein the step of immersing the metal in an electroless gold plating bath including a non-ammoniacal alkali metal hydroxide comprises the step of immersing the metal in an electroless gold plating bath including a non-ammoniacal alkali metal hydroxide selected from the group consisting of sodium hydroxide and potassium hydroxide.

5. A method as in claim 1 wherein the step of immersing the metal in an electroless gold plating bath including an organic chelating compound comprises the step of immersing the metal in an electroless gold plating bath including an organic chelating compound selected from the group consisting of tetra sodium ethylenediaminetetraacetate tetrahydrate, ethylenediamine, and triethanolamine.

6. A method as in claim 1 wherein the step of immersing the metal in an electroless gold plating bath comprises the step of immersing the metal in an electroless gold plating bath whose temperature is the boiling point temperature of said bath.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,862,850 Dated January 28, 1975

Inventor(s) Richard Kent Trueblood

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 12, cancel "process" and substitute -- processes --; line 34, cancel "molybenum" and substitute -- molybdenum --; and

Column 4, line 65, cancel "to", second occurrence, and substitute -- and --.

Signed and sealed this 8th day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
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